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Ion-exchange Equilibria between Solid Aluminium Pectinates and Ca, Mn^{II}, Cu^{II} and Fe^{III} Ions in Aqueous Solution

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The ion-exchange equilibria between solid aluminium pectinates and aqueous solutions of calcium, manganese, zinc, copper and iron(III) nitrates have been studied at 298 K. The equilibria are generically represented by the equation:

$$(z-i)\,\mathrm{Al(OH)_2P(s)} + \mathrm{M(OH)_i^{(z-i)+}(aq)} \rightleftharpoons \mathrm{M(OH)_i\,P_{(z-i)}(s)} + (z-i)\,\mathrm{Al(OH)_2^+(aq)}$$

where P is the active site of pectinates containing $(z-i)$ carboxy groups and their molecular surroundings, and $M(OH)_i^{(z-1)+}$ represents $Ca(OH)^+$, $Mn(OH)^+$, $Zn(OH)^+$, $Cu(OH)^+$, $Fe(OH)^+$ and $Fe(OH)^{2+}$. The equilibrium constants were determined using pectins with different degrees of methylation of the carboxy groups. The results are discussed in terms of interactions occurring in the ionic exchange for each of the metallic nitrates. Together with data from the literature it is possible to establish the following order of preference in bonding with pectins:

$$Fe^{III} > Al > Cu > Pb > Cd > Zn > Ni > Co > Sr \approx Ca \approx Mn > Mg.$$

The pectins are one of the main constituents of the vegetable cellular wall[1–6] and, because of the presence of the carboxylic group of D-galacturonates (the basic unit of the polymeric chain), they ought to play an important role in ion transport through the cellular wall by ionic exchange.[7–9]

Various properties of the pectins are dependent on the degree of methylation of the carboxylic groups. For instance, it was observed that calcium pectinate stability constants increase with the degree of methylation decreases.[10,11] For the formation of an 'egg-box' structure with calcium,[12,13] in addition to the degree methylation, the number of consecutive non-methylated carboxylic groups is also important.[14,15]

A large number of studies involving interaction between pectins, including cross-linked pectins (polymeric chain linked by methylene groups), pectic acid (pectin without methylated carboxylates) and metallic ions have been reported in the solid phase.[16–20] The goal of these studies was to determine the relative stability with different metal ions and the mode of binding of the metals (outer or inner coordination sphere). X-Ray diffraction of pectic acid,[1] sodium pectate[1] and calcium pectate[2] shows the presence of a helical polymeric chain. For calcium this helical structure is very different from the 'egg-box' structure exhibited in aqueous solution and gels.

In spite of the fact that aluminium pectinate, which is insoluble in water, has been known to exist for a long time, no quantitative study involving this compound has been reported. In acidic tropical soils aluminium is converted into a form toxic towards plants and crops.[7–21] In this paper we report a study of the ion-exchange equilibria between solid aluminium pectinate and aqueous calcium, manganese(II), zinc, copper(II) and iron(III) nitrate solutions at 298.2 K.

Table 1. Analysis of samples of pectins

sample	$n(-CO_2H)^a$ /10^{-3}(g pectin)$^{-1}$	D_M	b/pm	$\bar{M}_v$
1	1.151 ± 0.008	0.727 ± 0.003	1650	74 300 ± 1200
2	1.535 ± 0.006	0.638 ± 0.003	1240	69 200 ± 550
3	2.124 ± 0.003	0.498 ± 0.005	900	61 400 ± 550
4	2.52 ± 0.02	0.406 ± 0.003	760	56 100 ± 700

[a] $-CO_2H$ represents non-methylated carboxy groups.

Experimental

Reagents

Salts of analytical grade (Merck and Carlo-Erba) and citric pectin (Sigma) were used. The indicators used in metal spectrophotometric determinations were purified (chromoasurol-S[22] and eriochromecyanine-R[23,24]). Aluminon was prepared to avoid errors caused by impurities in commercial products.[25,26] The purity of doubly distilled water was monitored by conductivity measurements.

Preparation and Characterization of Pectins

The original pectin (sample 2, table 1) was purified,[6,10] methylated[27] or demethylated.[28] From this process four samples with different degrees of methylation were obtained (see table 1). The number of carboxy groups (free and methylated) was determined by potentiometric titrimetry.[29] The mean molar mass ($\bar{M}_v$) was determined by viscosity measurements.[30]

Preparation and Characterization of Aluminium Pectinates

Each pectin sample (0.4 g) was dissolved in water (100 cm^3) and the pH was adjusted to 3.8 by addition of sodium hydroxide. An aqueous aluminium chloride solution (0.1 mol dm^{-3}) was added until no more aluminium pectinate gel was precipitated (the pH was controlled by addition of sodium hydroxide).[31] The gel was filtered, washed with water until a negative chloride test was obtained, dried in vacuum over solid potassium hydroxide, ground and dried as before. The aluminium in these samples was determined by photometric back-titration of excess EDTA with standardized zinc chloride in a buffered medium[32] (pH 5.0). A gravimetric determination after calcination at 1200 °C was carried out on the pectinate obtained from the original pectin (sample 2)[31] and was in agreement with the former analysis.

The hydroxyl groups bound to aluminium were determined by reaction with fluoride in a hydrochloric acid solution (0.1 mol dm^{-3}). The hydroxide liberated by the reaction

$$-CO_2Al(OH)_n(s) + 6F^-(aq) = AlF_6^{3-}(aq) + nOH^-(aq) + -CO_2^-(aq)$$

reacted with the acid present and the excess acid was titrated potentiometrically.

Ion-exchange Experiments

Solid aluminium pectinate (20–110 mg) and aqueous solutions of the metallic nitrates were placed in polyethylene flasks (*ca.* 30 cm^3). The concentration intervals (mol dm^{-3}) were: Zn (0.5–4.5) × 10^{-2}, Fe^{III} (0.3–24.0) × 10^{-4}, Cu^{II} (0.3–3.4) × 10^{-2}, Ca (0.7–6.3) × 10^{-1}

and Mn^{II} (0.4–3.8) $\times 10^{-1}$. The pH was measured before and after the ion-exchange process and no correction was made. The flasks were submerged and shaken (25.0 $\pm$ 0.1 °C) in a thermostatted water bath. The following times (h) were required to reach equilibrium: Fe, 5; Cu, 12; Zn, 20; Mn, 50 and Ca, 70. The flasks were then allowed to stand without shaking for a few minutes in the water bath prior to decantation of the liquid phase. An aliquot of the supernatant was used to determine aluminium spectrophotometrically, with eriochromecyamine-R[33] (for exchange with Ca), cromoasurol-S[34] (for exchange with Zn and Mn) or with aluminon[25] (for exchange with Cu). Copper was previously eliminated from the solution by acidification with hydrochloric acid followed by precipitation with a stream of hydrogen sulphide.[35] In all cases the solid phase was filtered and dissolved in excess EDTA. This was then titrated photometrically with zinc chloride. In the ion exchange with Fe^{III} the iron in solution was determinated spectrophotometrically with *o*-phenantroline[36] after reduction with ascorbic acid. The total concentrations of iron and aluminium were determinated by photometric back-titration of excess EDTA with zinc chloride.[32]

Ion-exchange Thermodynamics

The thermodynamic equilibrium constant for the ion-exchange reaction:

$$z_B A^{z_A+}(aq) + z_A B^{z_B+}(s) = z_B A^{z_A+}(s) + z_A B^{z_B+}(aq)$$

can be defined as [37]

$$K^\theta = \frac{a_B^{z_A}(E_A g_A)^{z_B}}{a_A^{z_B}(E_B g_B)^{z_A}} = \frac{K_G g_A^{z_B}}{g_B^{z_A}} \quad (1)$$

where a_i and E_i are the activities and the equivalent fractions of the ions in the solution and solid phases, respectively, and g_i are the non-individual activity coefficients of the species i in the solid phase, they refer to a combination of species i with the exchanger in a fixed composition.

Applying the Gibbs–Duhem equation for all the species in the solid phase (A, B, H_2O) and using eqn (1) the following expression is obtained:[37,38]

$$\ln K^\theta = (z_B - z_A) + \int_0^1 \ln K_G \, dE_A + \Delta \quad (2)$$

$$\Delta = z_A z_B \left(\int_{a_w=1}^{a_w(B)} W_B \, d\ln a_w - \int_{a_w=1}^{a_w(B)} W_A \, d\ln a_w - \int_{a_w(A)}^{a_w(B)} W_{AB} \, d\ln a_w \right) \quad (3)$$

where K_G is the corrected selectivity quotient, W_i are the water contents (moles per exchange equivalent) of the exchanger in homoionic and mixture (AB) forms:

$$W_i = \frac{n_w^i}{z_A n_A + z_B n_B} \quad (4)$$

$a_w(A)$ and $a_w(B)$ are the activities of water when the exchanger in the homoionic form is equilibrated only with a solution containing, respectively, the salt of A^{z_A+} and B^{z_B+}, both at the same concentration.

Ion Exchange between Aluminium Pectinates and Metallic Nitrates

The ion-exchange equilibrium between aluminium pectinates and metallic nitrates in aqueous solution can be represented by

$$(z-i)\,Al(OH)_2\{P\}(s) + M(OH)_i^{(z-i)+}(aq) = M(OH)_i\{P\}(s) + (z-i)\,Al(OH)_2^+(aq) \quad (5)$$

where {P} represents the active site of pectinates constituted by carboxys and their molecular environment and $M(OH)^{(z-i)+}$ represent $CaOH^+$, $MnOH^+$, $ZnOH^+$, $CuOH^+$, $Fe(OH)^{2+}$ and $Fe(OH)_2^+$. The thermodynamic equilibrium constant can be defined as:

$$K^\theta = \frac{a_{Al(OH)_2}^{(z-i)}(E_{M(OH)_i} g_{M(OH)_i})}{a_{M(OH)_i}(E_{Al(OH)_2} g_{Al(OH)_2})^{(z-i)}} = K_G \frac{g_{M(OH)_i}}{g_{Al(OH)_2}^{(z-i)}}. \quad (6)$$

Owing to the impossibility of obtaining the relation between the mean ionic activity coefficients of the hydrolysed species, Γ:

$$\Gamma = \frac{\gamma_{Al(OH)_2^{+z-i}}}{\gamma_{M(OH)_i^{(z-i)+}}} = \frac{(\gamma^2_{\pm Al(OH)_2NO_3})^{z-i}}{\gamma^{(z-i+1)}_{\pm M(OH)_i(NO_3)_{(z-i)}}} \quad (7)$$

and therefore obtaining K^θ or K_G from eqn (6), the mean stoichiometric ionic activity coefficients of the metallic nitrates and the stoichiometric concentrations

$$C_M = \sum_{i=0} [M(OH)_i^{(z-i)+}]$$

of the ions were utilized in determining the stoichiometric equilibrium constant, K_e:

$$K_e = \frac{C_{Al}^{z-i} E_M}{C_M E_{Al}^{z-i}} \Gamma_e \frac{g_M}{g_{Al}^{z-i}} \quad (8)$$

where

$$\Gamma_e = \frac{(\gamma^2_{\pm Al})^{z-i}}{\gamma^{z-i}_{\pm M}}. \quad (9)$$

Γ_e refers to the relation between the mean stoichiometric ionic activity coefficients in the mixture of electrolytes, obtained using Brønsted's theory of specific ion interaction,[39] revised by Harned and Robinson.[40]

From eqn (2) the stoichiometric equilibrium constant is:

$$\ln K_e = [1-(z-i)] + \int_0^1 \ln K \, dE_M + \Delta. \quad (10)$$

When $\ln K$ is a linear function of E_M, the integration of $\ln K dE_M$ reduces to an interpolation of K to $E_M = 0.5$ (mean value of the function). Then, $K_e = K\{E_M = 0.5\}$. A linear function was obtained except in the case of Mn, where a negligibly small deviation occurred. The calculation of K_e depends on Δ and, under these conditions, this quantity may be considered to be negligible.

Evaluation of Δ for the Ion Exchange between Aluminium Pectinates and Metal Nitrates

During ion exchange between aluminium pectinates and metal nitrates, no increase of the solid volume was observed. Therefore we may assume that the water contents in the exchanger in the homoionic and mixture forms undergo little variation with the water activity in the solution. Based on the above considerations, and applying the mean-value theorem, the following equation can be written:[37]

$$\Delta = (z-i)\left(W_{Al} \ln a_w(Al) - W_M \ln a_w(M) - \bar{W}_{M,Al} \ln \frac{a_w(Al)}{a_w(M)}\right) \quad (11)$$

where

$$\bar{W}_{M,Al} = (W_{Al} + W_M)/2.$$

The exchange was generally carried out in dilute solutions and we may assume that $a(Al) \approx a_w(M) \approx a_w$. Under these conditions the values of Δ are small ($a_w \to 1$) when compared with $\ln K_e$ in eqn (11) or with the experimental accuracy.

Activity Coefficients

The mean ionic activity coefficients for copper, zinc and calcium nitrates were obtained from the literature.[41–43] The coefficients for manganese and iron(III) nitrates were calculated using the data for effective ionic size of the hydrated ions.[44]

For aluminium nitrate the activity coefficient was obtained from vapour pressure data[45,46] using, however, a more critical value of the water vapour pressure.[47] The following expressions were used:

$$\ln \gamma_{\pm} = (\phi - 1) + 2\int_0^m (\phi - 1)\, m^{-\frac{1}{2}}\, \mathrm{d}m^{\frac{1}{2}} \qquad (12)$$

and

$$\phi = -(1000/\nu m M)\{\ln [P(m)/P^0] + B|P(m) - P^0|/RT\} \qquad (13)$$

where ϕ is the osmotic coefficient, m is the molality of the solution (mol kg^{-1}), ν is the number of ions per formula of the dissociated electrolyte ($=4$), M is the molar mass of the solvent, $P(m)$ is the vapour pressure for a solution of molality m, P^0 is the vapour pressure of pure water (3.1685 kPa at 298.15 K) and B is the second virial coefficient for water vapour. The value of $(\phi - 1)\, m^{-\frac{1}{2}}$ was calculated from the Debye–Hückel limiting law when $m = 0$.

The activity coefficients, calculated or from the literature, refer to pure electrolytes. The mean ionic activity coefficients in the mixture of aluminium nitrates with other metal nitrates ($\gamma_{\pm}$) were also calculated by applying Brønsted's theory,[39] considering the specific interaction, as reviewed in depth by Harned and Robinson.[40]

Mean Distance between Carboxy Groups of the Pectinates

The mean distance (b) between carboxy groups of metal pectinates, which behave as linear, reasonably rigid macromolecules, can be calculated according to[48]

$$b = b_0/(1 - D_M)$$

where b_0 is the mean distance between neighbouring carboxy groups in the macromolecule of pectic acid ($D_M = 0.0$), where D_M is the degree of methylation.

$b_0 = 450$ pm was determined by X-ray diffraction of fibrous sodium pectate,[1] pectic acid[1] and gels of pectinic acid and sodium pectate.[2] Table 1 shows the values of b_0 calculated for the four pectins.

Results and Discussion

Analysis of Samples of Pectins and Aluminium Pectinates

The analytical results of table 2 refer to samples of aluminium pectinates, obtained from pectins with different degrees of methylation. The mean molar mass, $\bar{M}_v$ (table 1), was obtained by viscosity measurements. Potentiometric analysis showed that there were $(4.23 \pm 0.04) \times 10^3$ mol of carboxy groups (methylated and non-methylated) per gram of pectin. The relations $n(\mathrm{Al})/n(\mathrm{CO_2^-})$ and $n(\mathrm{OH})/n(\mathrm{Al})$ for sample 2 show that all the active sites of the pectin were saturated by aluminium. The results show that the carboxy groups are the only active sites and that they are occupied by Al(OH) species. The observed values of the relation $n(\mathrm{Al})/n(\mathrm{CO_2^-})$ for other samples indicate that the substitutions were not complete. In these cases a correction in the calculation of the relation $n(\mathrm{OH})/n(\mathrm{Al})$ was made since the remaining acid groups interfere in the hydroxy determinations. The values $n(\mathrm{OH})/n(\mathrm{Al})$ for the samples, which were already corrected, are also close to 2, as for sample 2.

Table 2. Stoichiometry between the aluminium and non-methylated carboxy groups and between the hydroxy and aluminium on the aluminium pectinates

sample	$n(-CO_2^-)/10^{-3}$ (g PA1)$^{-1}$	$n(Al)/10^{-3}$ (g PA1)$^{-1}$	$n(OH)/10^{-3}$ (g PA1)$^{-1}$	$n(Al)/n(-CO_2^-)$	$n(OH)/n(Al)$	$n(OH)/n(Al)_{corr.}$
1	1.077±0.008	0.98±0.03	1.78±0.01	0.91±0.03	1.82±0.06	1.9±0.1
2	1.406±0.006	1.40±0.01	2.90±0.04	0.99±0.01	2.07±0.04	2.07±0.04
3	1.884±0.003	1.564±0.005	2.73±0.02	0.83±0.03	1.75±0.002	1.95±0.04
4	2.19±0.02	1.922±0.005	3.52±0.03	0.878±0.008	1.83±0.02	1.97±0.04

Table 3. Equilibrium constants K_e (see text) for the ion exchange between solid aluminium pectinates (PA1) and metal nitrates

sample	Ca 10^3K_e	Mn 10^3K_e	Zn 10^2K_e	Cu K_e	Fe K_e
1	1.9±0.2	3.0±0.4	3.1±0.2	0.12±0.02	37±2
2	1.4±0.2	1.9±0.2	2.8±0.3	0.13±0.01	44±5
3	0.7±0.1	1.1±0.2	2.0±0.3	0.11±0.01	34±2
4	1.0±0.1	1.3±0.1	2.0±0.3	0.11±0.03	0.012±0.002

Ion Exchange

The results of the ion-exchange experiments are given in the table 3. Fig. 1 and table 4 show the results of ion exchange with zinc nitrate for sample 2.

In the ion exchange between the four samples of aluminium pectinates and calcium, zinc, manganese and copper nitrates the $Al(OH)_2^+$ was substituted by the MOH^+ species. In the ion exchange with iron(III) the $Al(OH)_2^+$ of samples 1–3 was substituted by $Fe(OH)_2^+$, while in sample 4 the substitution occurred with $FeOH^{2+}$, giving a CO_2^-:Fe ratio of 2:1. The metals were analysed in the solid and liquid phases and the protonated carboxys remaining in the aluminium pectinates were not substituted by other ionic species.

Beyond the principal interaction, *i.e.* metal ions with carboxys, other interactions such as the cooperative effect, site proximity, multisite bonding, solid-phase heterogeneity, the degree of methylation of the pectins, the pH, water adsorption by the solid and interactions in the solution can also affect the K_e values.

The water adsorption in the solid phase was analysed in detail by considering the part played by 'ion-exchange thermodynamics' and can be considered to be negligible in the ion exchange between aluminium pectinates and metal nitrates.

In nearly all cases for the ion-exchange processes the pH variation was small over the whole ionic concentration interval. This does not explain why the process is insensitive to pH, but confirms the ion-exchange equilibrium represented by eqn (5). For iron(III) a larger inverval of pH (3.24–4.15) was observed.

In all cases, with the exception of manganese, the results show a linear increase of $\ln K$ with E_M. This is the reverse of that found between experiments of ion exchange between cross-linked potassium pectate and metal salts,[20] where $\ln K$ decreases with E_M. In our system it is necessary to consider the cooperative effect and solid-phase heterogeneity. The cooperative effect suggests that $\ln K$ increases with E_m; however, heterogeneity can cause either increases or decreases in $\ln K$. Thus, the linear increase in $\ln K$ with E_M observed for ion exchange with Ca, Zn and Cu is probably due to the cooperative effect. In the ion exchange with Mn the heterogeneity might contribute, and

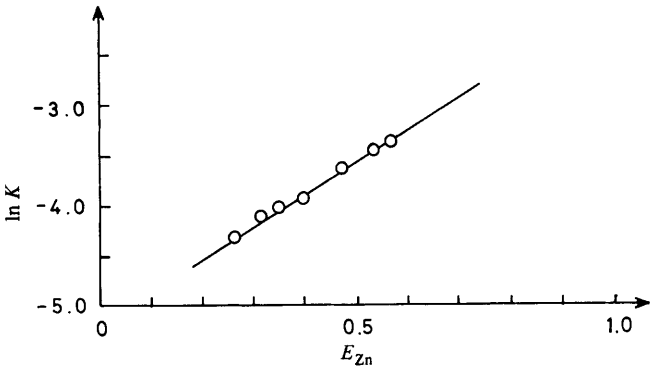

Fig. 1. Plot ($\ln K, E_{Zn}$) for ion-exchange equilibria between solid aluminium pectinate and zinc nitrate (sample 2).

Table 4. Ion-exchange equilibria between solid aluminium pectinate (PA1) and zinc nitrate (sample 2)

m(PA1) /mg	$C_{Zn}/10^{-2}$ mol dm^{-3}	$C_{Al}/10^{-4}$ mol dm^{-3}	E_{Zn}	E_{Al}	$\gamma_{\pm Zn}$	$\gamma_{\pm Al}$	10^2K_e	pH
72.8	1.90	10.86	0.267	0.733	0.666	0.538	1.36	4.06
72.56	2.44	12.86	0.317	0.683	0.644	0.506	1.51	4.02
78.29	2.78	15.48	0.354	0.646	0.632	0.488	1.82	4.0
75.9	3.25	16.9	0.399	0.601	0.618	0.468	1.98	4.0
75.15	4.23	22.44	0.535	0.465	0.595	0.433	3.24	4.02
93.05	4.55	27.35	0.564	0.474	0.587	0.422	3.45	4.02
76.85	3.67	20.23	0.471	0.529	0.607	0.451	2.72	4.0

in the exchange process with Fe, other effects could be present, in spite of the linearity.

The proximity of sites can be considered to be of little importance. In sample 4, which has a low degree of methylation, a mean distance between the carboxys of 760 pm was found, which is large compared to the ionic radii. Additionally, K_e values vary slightly with the degree of methylation, which would not be observed if a site-proximity effect was important.

Except for the case of iron(III), which is discussed below, multisite bonding was not considered. The stoichiometry of the aluminium pectinate preparations shows very well that each ion binds to a specific site.

The interionic interaction in solution can effect the equilibria and Γ_e should be corrected for these effects. In the cases of Cu, Zn and Fe, the solutions were sufficiently dilute and the variations of K_e observed for Zn and Fe ought not be due to these interactions. For Ca and Mn, where higher concentrations were used, the interactions seem to be more appreciable. Nevertheless, our data involving mixed electrolytes are too limited to permit a good evaluation of these effects, because Brønsted's method of specific interaction is only valid for dilute solutions. If so, the variations of K_e are also reflected by the interactions in solution.

In the cases of Zn, Ca and Mn a tendency of K_e to increase with the degree of methylation was observed, even though an inversion occurred in samples 3 and 4 for Ca and Mn. This is the same tendency observed for K as a function of E_M. The decrease in

disposable sites favours ion exchange. In view of the many factors which affect K_e, it is not possible to explain this inversion.

The iron(III) pectinate in sample 4 undergoes substitution of two species of charge +1 for each one of charge +2. This process causes a change in the solid-phase structure. Probably, the iron(III) pectinate (sample 4) has one interpolymeric structure involving two different carboxy chains. Intrapolymeric bonding is less probable because the mean distances between the carboxys (see table 1) ought to be greater than the sum of the Fe^{3+} ionic radius and the covalent radii of O and H, which amounts to 167 pm (the Fe–OH distance found in goethite is 212 pm),[49] also the effects already discussed other of smaller importance, such as water adsorption, site proximity and solution interactions, can also be considered and these other effects can influence the values of K_e. Nevertheless, it was also observed that the substitution of Al by other ions increases with the decrease of the available sites for exchange.

Conclusion

By using the results listed in table 3 and selectivity coefficients from the literature for ion exchange between cross-linked potassium pectate and various ions[20] a sequence of affinities between the carboxy group, its molecular environment and the various ions in aqueous solution can be established:

$$Fe^{III} > Al > Cu > Pb > Cd > Zn > Ni > Co > Sr \approx Ca \approx Mn > Mg.$$

It is possible to calculate the ion-exchange constant (K_1) for cross-linked pectates (P′)

$$Ca\{P'\}_2 + Cu^{2+}(aq) = Cu\{P'\}_2(s) + Ca^{2+}(aq); \quad K_1 = 27.3.$$

The data of table 3 can also be used to calculate ion exchange in pectinates:

$$Ca(OH)\{P\}(s) + Cu(OH)^+(aq) = Cu(OH)\{P\}(S) + Ca(OH)^+(aq); \quad K_2 = 96.0.$$

It is worth noting that $K_2 > K_1$; *i.e.* cross-linking makes the interaction of ions with the active centres more difficult, when compared with pectates without cross-linking.

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